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TECHNICAL REPORT No. 90

Laser-Induced Metal Deposition on Semiconductors From Liquid Electrolytes

by

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Prepared for Publication

in

Applied Physics Letters

Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

December 1988

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REPORT DOCUMENTATION PAGE

Form Approved
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2b. DECLASSIFICATION / DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/88/TR-90			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York		6b. OFFICE SYMBOL (If applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260			7b. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217			10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.		PROJECT NO.	TASK NO.
					WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Laser-Induced Metal Deposition on Semiconductors From Liquid Electrolytes					
12. PERSONAL AUTHOR(S) L. Nánai, I. Hevesi, F. V. Bunkin, B. S. Luk'yanchuk, M. R. Brook, G. A. Shafeev, Daniel A. Jelski, Z. C. Wu and Thomas F. George					
13a. TYPE OF REPORT		13b. TIME COVERED FROM _____ TO _____		14. DATE OF REPORT (Year, Month, Day) December 1988	
				15. PAGE COUNT 15	
16. SUPPLEMENTARY NOTATION Prepared for publication in Applied Physics Letters					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	MASKLESS DEPOSITION, LIQUID ELECTROLYTES,		
			LASER-INDUCED, MICRON LATERAL DIMENSIONS,		
			METAL, ONTO SEMICONDUCTORS, DEMBER EFFECT, Gallium Arsenides		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Maskless deposition of gold and copper from electrolyte solutions onto n-doped semiconductors (GaAs, Si) is investigated. The metal deposits are found to have lateral dimensions of about 1 μ m and are in barrier contact with the semiconductor. The proposed deposition mechanism is governed by the electric fields resulting from the Dember effect, the p-n junction and the thermal emf. <i>Silicon, (n-gm)</i>					
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson			22b. TELEPHONE (Include Area Code) (202) 696-4410		22c. OFFICE SYMBOL

LASER-INDUCED METAL DEPOSITION ON SEMICONDUCTORS FROM LIQUID ELECTROLYTES

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ABSTRACT

Maskless deposition of gold and copper from electrolyte solutions onto n-doped semiconductors (GaAs, Si) is investigated. The metal deposits are found to have lateral dimensions of about $1\ \mu\text{m}$ and are in barrier contact with the semiconductor. The proposed deposition mechanism is governed by the electric fields resulting from the Dember effect, the p-n junction and the thermal emf.

PACS: 81.15Lm, 68.55t6, 42.60



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I. Introduction

Laser-induced microchemistry is one of the most important alternative methods for the fabrication of different electronic devices.^{1,2} Maskless laser-induced deposition of metals onto semiconductor surfaces is a field of growing interest because of the necessity to provide well-localized ($1\ \mu\text{m}$) deposits with good conductivity, and with a controllable type of contact (ohmic or barrier). Deposition from both gaseous³⁻⁷ and liquid⁸⁻¹⁰ phases has advantages and disadvantages, depending on the application.

Until now, two mechanisms for laser-induced metal deposition have been described for electrolytes containing metal salts:

- 1) photochemical mechanism,^{11,12}
- 2) thermal decomposition mechanism.^{13,14}

In this paper we present experimental results concerning metal deposition onto semiconductors from liquid electrolytic solutions. The advantage of the present method is that it is a simple technique which produces quality, reproducible results. It is also amenable to theoretical treatment, which will be the subject of a subsequent paper.¹⁵

II. Experimental Procedure

The experimental setup is shown schematically in Fig. 1. We used a copper vapor laser in a projection microscopic configuration, which also initiated the deposition.¹⁶ This setup permitted the real-time observation of the deposition process on a screen, with linear magnification of about 1000-fold. The laser pulses ($\lambda = 510.6\ \text{nm}$, $f = 10\ \text{kHz}$, $\tau_{\text{pulse}} = 20\ \text{ns}$) had an average power 1-5 mW and were focused on the semiconductor wafer surface. The spot size diameters were in the range $1 - 10\ \mu\text{m}$. The samples (n-Si and n-GaAs

with $n = 10^{18} \text{ cm}^{-3}$) were put into a dielectric cell filled with the metal salt solution [CuSO_4 or $\text{KAu}(\text{CN})_2$ standard electrolyte]. No external electric field was used in our experiments. A computer-driven x-y stage allowed the appropriate scanning and positioning. The samples with deposits were submitted for mechanical, microscopical and electrical investigations.

III. Results

A. Deposition of Gold

Single crystalline n-type GaAs wafers with parallel 100 surfaces and without any precoating were used. Among many possible electrolytes, $\text{KAu}(\text{CN})_2$ was found to yield the best results for gold deposition.

The diameter of deposits at the initial stage of the process were found to be much smaller than the laser beam diameter. The main part of the deposit (nearly 80%) appears within 10-50 ms, and with a 1 sec exposure time the deposit diameter reaches that of the laser beam. Thus the deposition rate decreases very dramatically with time.

The morphology of the deposit depends on the laser beam diameter. Deposits with lateral dimensions of about $1 \mu\text{m}$ appear as a succession of structureless hemispheres, as shown in Fig. 2a. When the laser beam diameter is on the order of a few μm , a well-defined gap forms in the middle of the deposited region (Fig. 2b). For even larger focal points, the middle part of the strip is filled with spherical metal particles.

Energy dispersive analysis by X-rays reveals no contamination, indicating purity to within the 1% accuracy of the instrument (K, L and M lines). The deposits prepared by this method represent rectifying contact

with GaAs with a typical barrier height of 0.9 V. The conductivity of the obtained strips was found to be 2-3 times less than that of bulk gold.

B. Deposition of Copper

Deposition of copper was carried out via the same technique as gold, using CuSO_4 in aqueous solution. Figures 2c and 2d show typical results of copper deposits on GaAs and Si, respectively. Copper deposition on silicon was successful provided HF was present in the electrolyte ($\text{pH} = 1.5$). In this case, a uniform copper film adsorbed loosely onto the Si surface even in the absence of laser radiation. Turning on the laser yields an accelerated deposition process with good adhesion (scotch test).

The conductivity of copper deposits on both substrates depends on the scanning speed. At the slowest speed ($v = 20 \mu\text{m/s}$) it is half the value of the bulk material. At $v = 100 \mu\text{m/s}$ it is one-sixth that of bulk copper. At high scanning speeds the effects of a single laser pulse can be observed. The resulting deposit has a typical height of $0.1 \mu\text{m}$ (Cu on GaAs at $P \approx 5 \text{ mW}$). Formally the deposition speed is $10^6 \mu\text{m/s}$, though it decreases after the first shot to $10 \mu\text{m/s}$. Finally, the deposition width also depends on the scanning speed, as shown in Fig. 3. At an increasing scan rate, both the height and the volume of the deposit decrease slowly (Fig. 4).

We were unable to deposit either copper or gold on either p-GaAs or p-Si. Only intensive etching was observed in the illuminated area.

IV. Discussion

The photochemical deposition mechanism is known to be successful for metals with a negative electrode potential, such as zinc, cadmium or nickel. This kind of deposition is probably only possible on p-type semiconductor

wafers.^{11,12} For electrodeless deposition, the laser illumination creates a cathodic region in the illuminated area and an anodic region elsewhere. For the p-type semiconductor, the cathodic deposition reaction occurs in the conduction band through the light-produced carriers. Conversely, the anodic metal stripping takes place in the valence band in the dark region.

Considering the experimental conditions for GaAs, it is clear that each laser pulse produces nonequilibrium carriers with energies $E \approx h\nu - E_g \approx 1.7$ eV. These transmit their energy to the lattice, resulting in a temperature increase of about 20 K, which corresponds to a thermal emf between the heated and non-heated areas of about 80 mV. We note that in the case of n-GaAs the holes remain in the irradiated region; electrons move outside. The potential difference (the Dember photo emf U_D) due to their different mobilities ($\mu_e/\mu_h \approx 8$ for GaAs) is approximately the same order of magnitude as the thermal emf. The value of U_D depends on the generation rate g_s and is about 200-300 mV. Its rise time ($t_{rD} \approx d_B^2/D_a = 2.10 \times 10^{-8}$ s where D_a is the diffusion coefficient $50 \text{ cm}^2/\text{s}$) is comparable to the laser pulse duration.

In n-type wafers the thermal emf and U_D are combined into a p-n junction at the electrolyte-wafer interface. Therefore, in the centers which are enriched in holes, the anodic reaction takes place (semiconductor etching). Outside we have an electron-rich ring-shaped region in which the cathodic reaction takes place. A similar situation occurs for gold deposition from KAu(CN)_2 . After the formation of an initial ring-shaped deposit (with proven barrier contact), the generated carriers are separated by a p-n junction field ($\sim 1\text{V}$ at a few μm distance) and the deposition process takes place in the center also. Ring-shaped deposits are observed with relatively weak solutions

(0.04 M CuSO_4). This deposition process can be stopped by imposing an electric field of appropriate polarity, as has been verified experimentally.

Acknowledgments

The European authors are indebted to Dr. S.V. Lavrishev for helpful assistance in studying deposit morphology, and also Prof. Dr. S.V. Gaponov for stimulating the present work. The American authors acknowledge the Office of Naval Research and the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, for support of their research.

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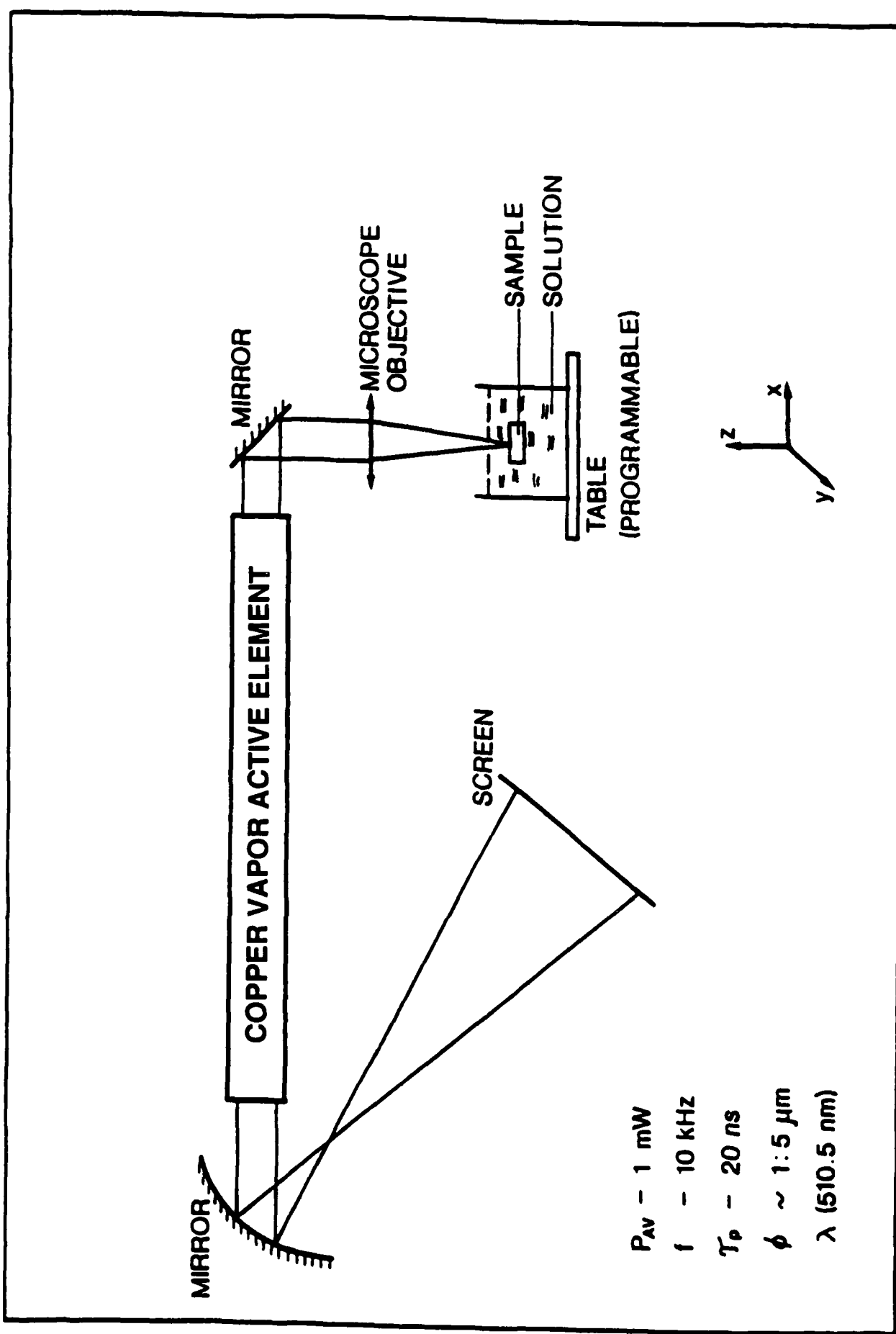
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FIGURE CAPTIONS

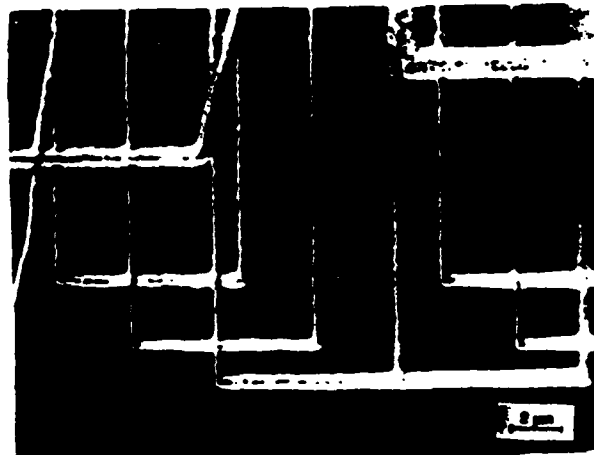
- Fig. 1. Schema of the experimental apparatus.
- Fig. 2. Photos of deposits: (a) Au(nGaAs) "hemispheres"; (b) Au(nGaAs) with a gap in the middle of the deposited strip; (c) Cu(nGaAs) deposit; (d) Cu(nSi) deposit.
- Fig. 3. Dependence of the deposit width on scanning speed for Cu(nGaAs); $P_a = 6$ mW, $P_b = 8$ mW and $P_c = 10$ mW. Similar results obtain for copper deposited on silicon. The curves represent a least squares fit to the data.
- Fig. 4. Dependence of the deposit volume on scanning speed for Cu(nGaAs); $P_a = 6$ mW, $P_b = 8$ mW and $P_c = 10$ mW. The curves are a least squares fit to the data.

Fig. 1

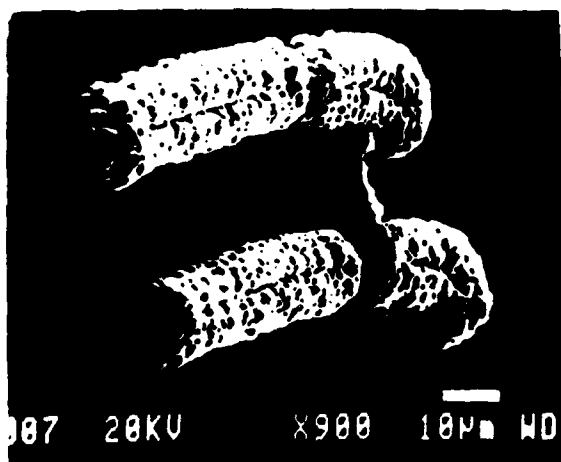




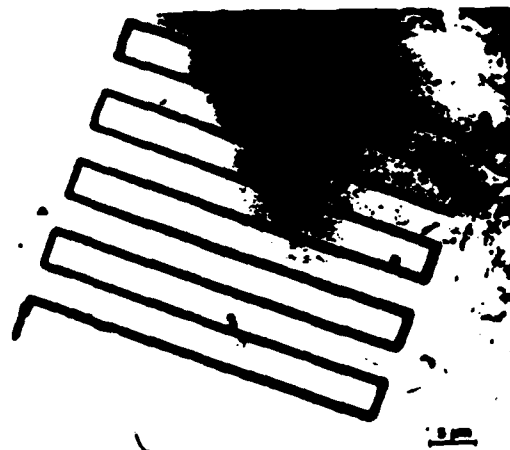
(a)



(b)



(c)



(d)

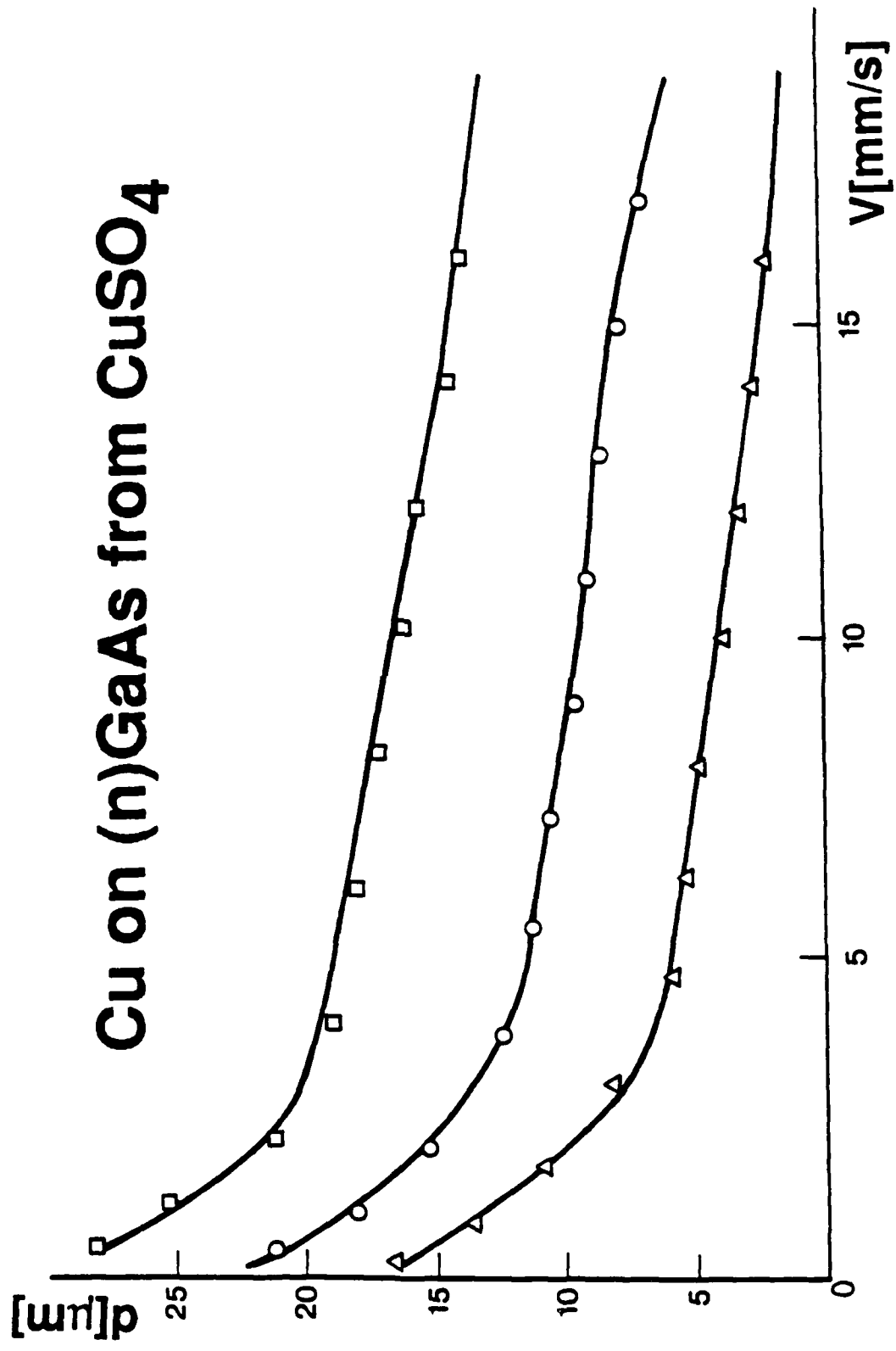


Fig. 3

Cu on (n)GaAs from CuSO_4

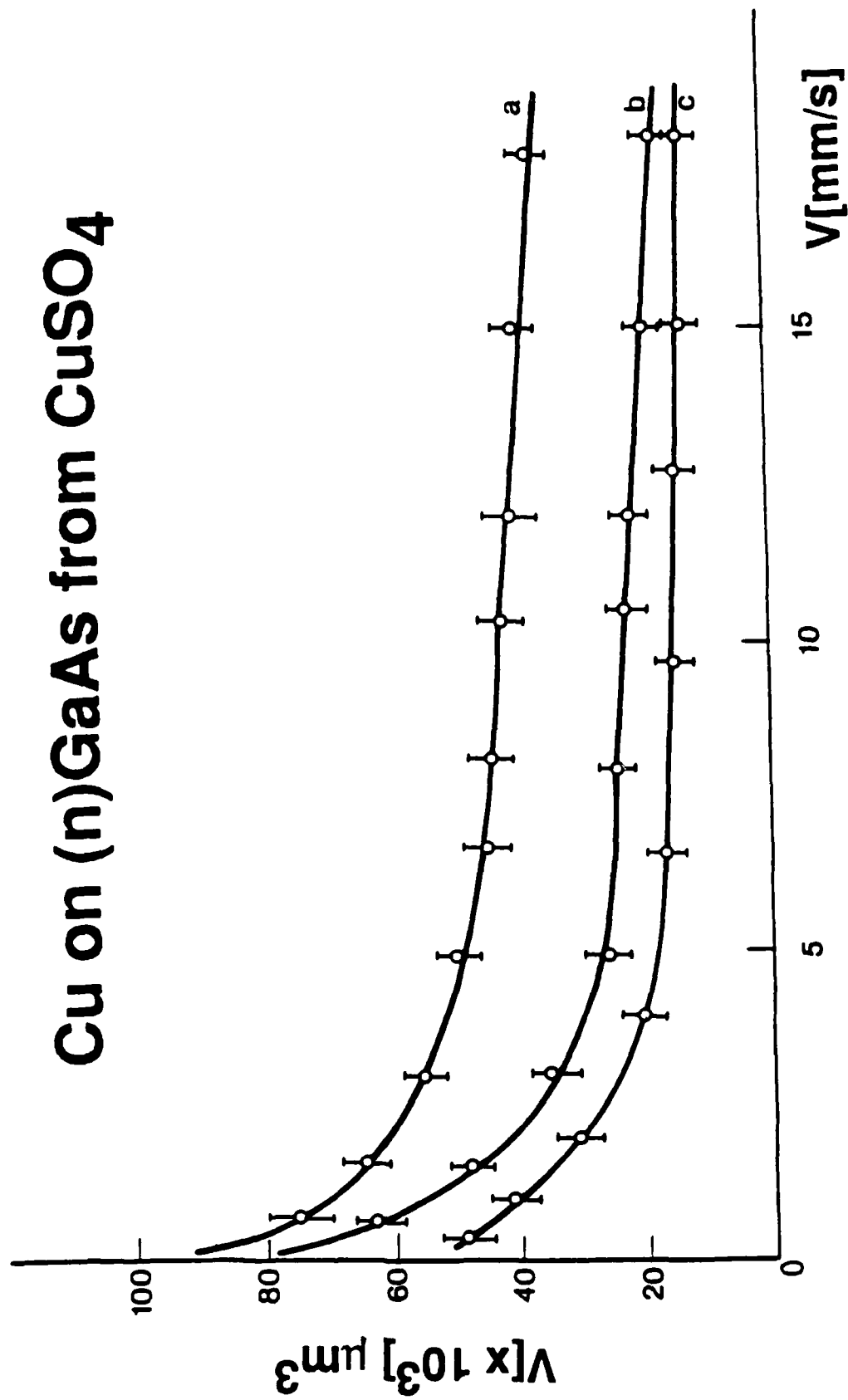


Fig. 4

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